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(54) Title: SULFONATED COPOLYMER

(57) Abstract: This invention relates to sulfonated copolymers which are useful in forming polymer electrolyte membranes used in fuel cells.



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SULFONATED COPOLYMER

TECHNICAL FIELD

This invention relates to sulfonated copolymers which are useful in forming polymer electrolyte membranes used in fuel cells.

5 BACKGROUND OF THE INVENTION

Fuel cells have been projected as promising power sources for portable electronic devices, electric vehicles, and other applications due mainly to their non-polluting nature. Of various fuel cell systems, the polymer electrolyte membrane based fuel cell technology such as direct methanol fuel cells (DMFCs) has attracted much interest thanks
10 to their high power density and high energy conversion efficiency. The “heart” of a polymer electrolyte membrane based fuel cell is the so called “membrane-electrode assembly” (MEA), which comprises a proton conducting polymer electrolyte membrane (PEM), catalyst disposed on the opposite surfaces of the PEM to form a catalyst coated member (CCM) and a pair of electrodes (*i.e.*, an anode and a cathode) disposed to be in
15 electrical contact with the catalyst layer.

Proton-conducting membranes for DMFCs are known, such as Nafion® from the E.I. Dupont De Nemours and Company or analogous products from Dow Chemicals. These perfluorinated hydrocarbon sulfonate ionomer products, however, have serious limitations when used in DMFC's. Nafion® loses conductivity when the operation temperature of
20 the fuel cell is over 80°C. Moreover, Nafion® has a very high methanol crossover rate, which impedes its applications in DMFCs.

U.S. Patent No. 5,773,480, assigned to Ballard Power System, describes a partially fluorinated proton conducting membrane from α , β , β -trifluorostyrene. One disadvantage of this membrane is its high cost of manufacturing due to the complex synthetic processes for monomer α , β , β -trifluorostyrene and the poor sulfonation ability of poly (α , β , β -trifluorostyrene). Another disadvantage of this membrane is that it is very brittle, thus has to be incorporated into a supporting matrix.

U.S. Patent Nos. 6,300,381 and 6,194,474 to Kerres, et al. describe an acid-base binary polymer blend system for proton conducting membranes, wherein the sulfonated poly(ether sulfone) was made by post-sulfonation of the poly (ether sulfone).

M. Ueda in the Journal of Polymer Science, 31(1993): 853, discloses the use of sulfonated monomers to prepare the sulfonated poly(ether sulfone polymers).

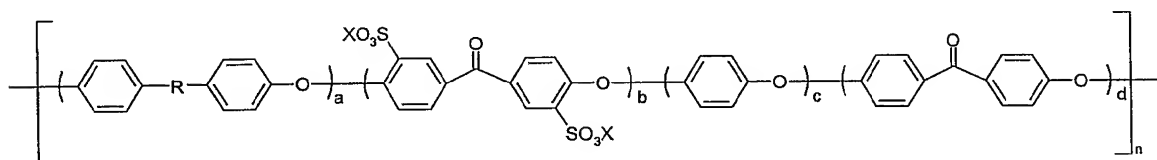
U.S. Patent Application US 2002/0091225A1 to McGrath, et al. used this method to prepare sulfonated polysulfone polymers.

The need for a good membrane for fuel cell operation requires balancing of various properties of the membrane. Such properties included proton conductivity, methanol-resistance, chemical stability and methanol crossover, fast start up of DMFCs, and durability to cell performance. In addition, it is important for the membrane to retain its dimensional stability over the fuel operational temperature range. In DMFC's methanol oxidation generates enough heat to raise the cell temperature. If the membrane swells significantly, it will increase methanol crossover. The membrane thus gradually loses its ability to block methanol crossover, resulting in degradation of cell performance. The dimension changes of the membrane also put a stress on the bonding of the membrane-electrode assembly (MEA). Often this results in delamination of the membrane from the electrode after excessive swelling of the membrane. Therefore, maintaining the dimensional stability over a wide temperature range and avoiding excessive membrane swelling are important for DMFC applications.

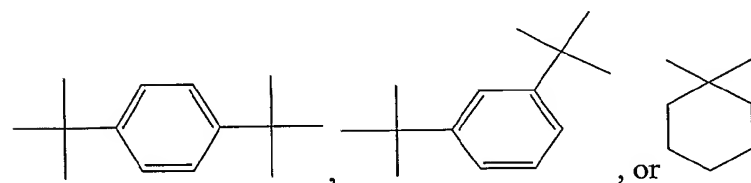
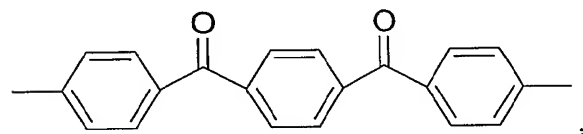
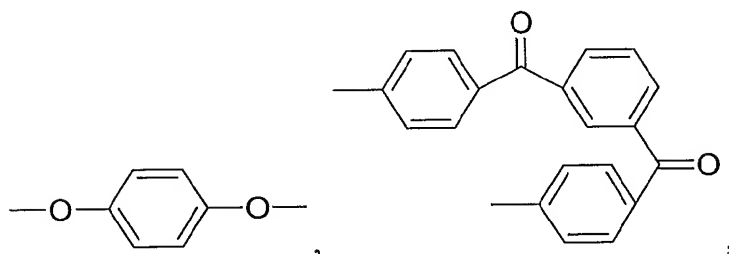
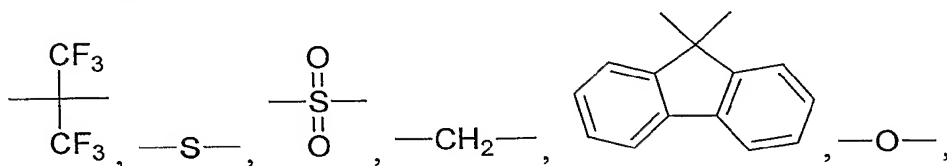
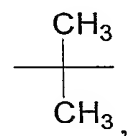
SUMMARY OF THE INVENTION

In one aspect, the invention provides sulfonated random copolymer compositions which can be used to fabricate polymer electrolyte membranes (PEM's), catalyst coated membrane (CCM's) and membrane electrode assemblies (MEAs) which are useful in fuel cells.

- 5 The invention includes two classes of random sulfonated copolymers. Such random polymers are of either of the following formulas:

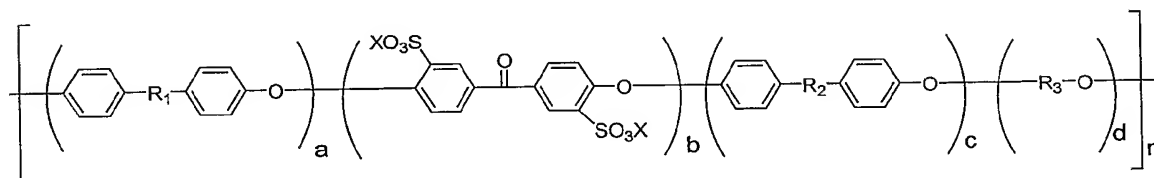


wherein R is a single bond, a cycloaliphatic of the formula C_nH_{2n-2} ;

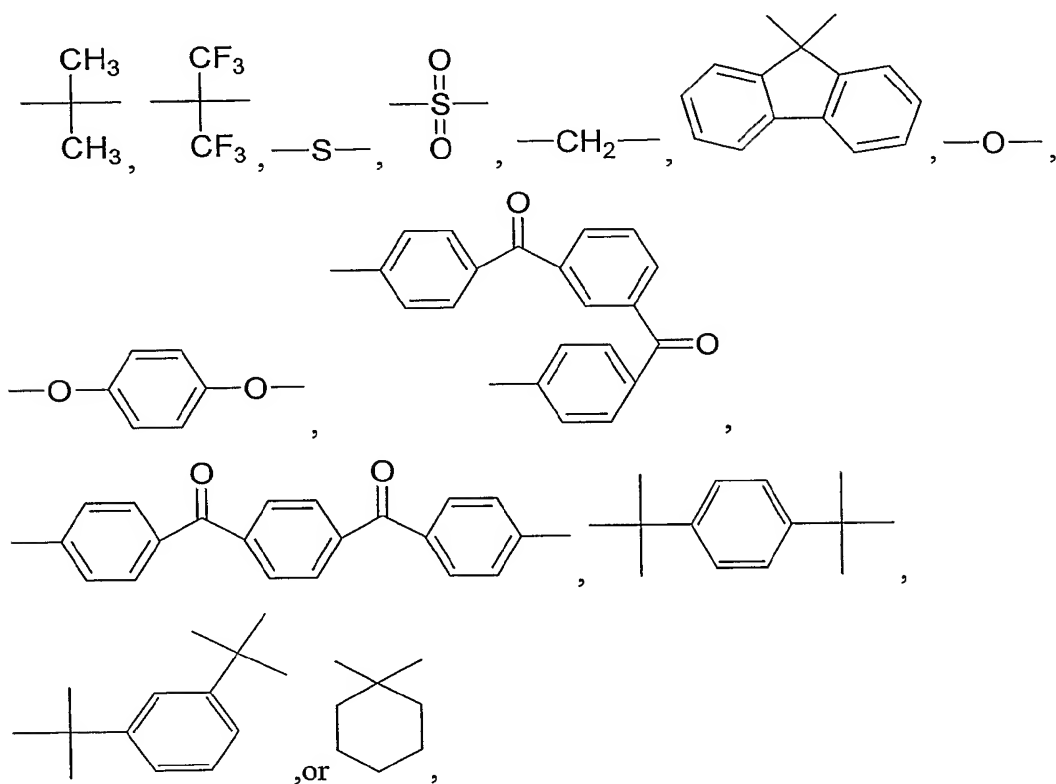


wherein a, b, c and d are mole fractions of the monomer present in the copolymer where each are independently, from 0.01 to 1; and

wherein X is a cation or a proton.



5 wherein R1 or R2 are independently a single bond, a cycloaliphatic of the formula C_nH_{2n-2} ,



where R3 is aryl ketone, aryl sulfone, aryl nitrile, and substituted aryl nitrile;

wherein a, b, c and d are mole fractions of the monomer present in the copolymer where each are independently, from 0.01 to 1; and

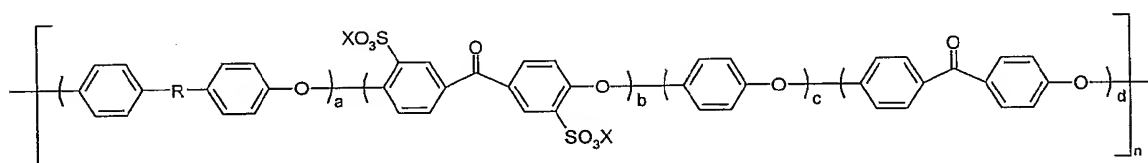
wherein X is a cation or a hydrogen atom.

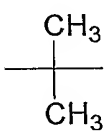
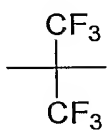
DETAILED DESCRIPTION

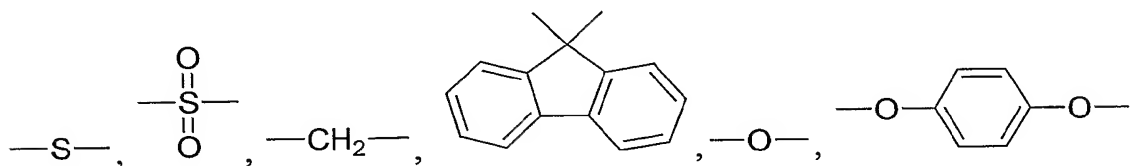
The invention provides random sulfonated copolymers. One use of such polymeric material is in the formation of polymer electrolyte membranes (PEMs), catalyst coated membrane (CCM) and membrane electrode assemblies (MEA's), which may be used in fuel DMFC's fuel cells.

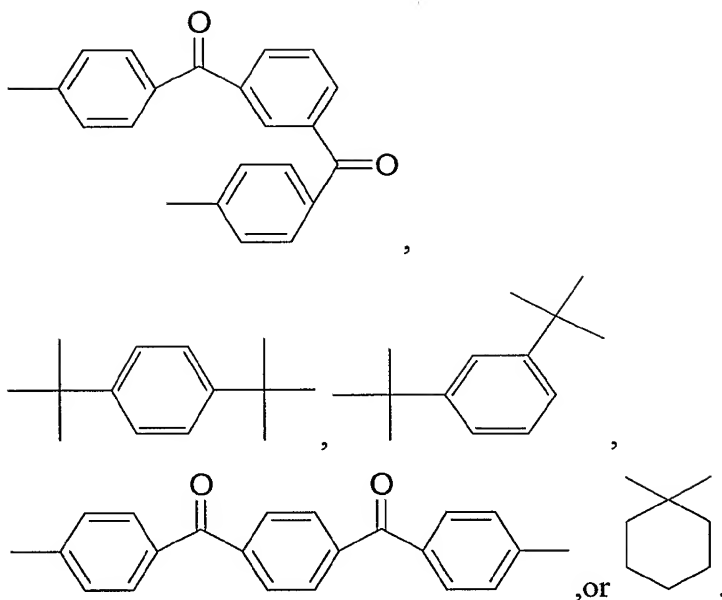
In one embodiment, sulfonated copolymers can be made having the following formula:

I



wherein R is a single bond, a cycloaliphatic of the formula C_nH_{2n-2} , , ,



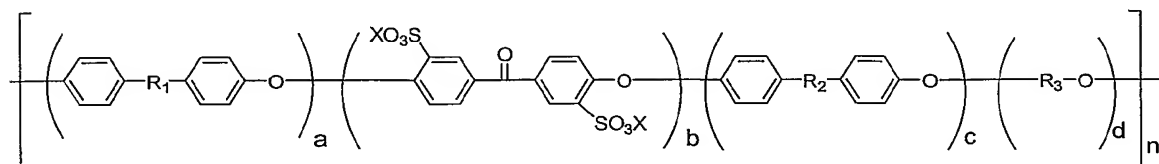


In the sulfonated copolymer, a, b, c and d are mole fractions of each of the monomers present in the copolymer where each are independently, from 0.01 to about 1, and X is a cation or a proton. In one particular embodiment, R is isopropylidene or cyclohexylidene.

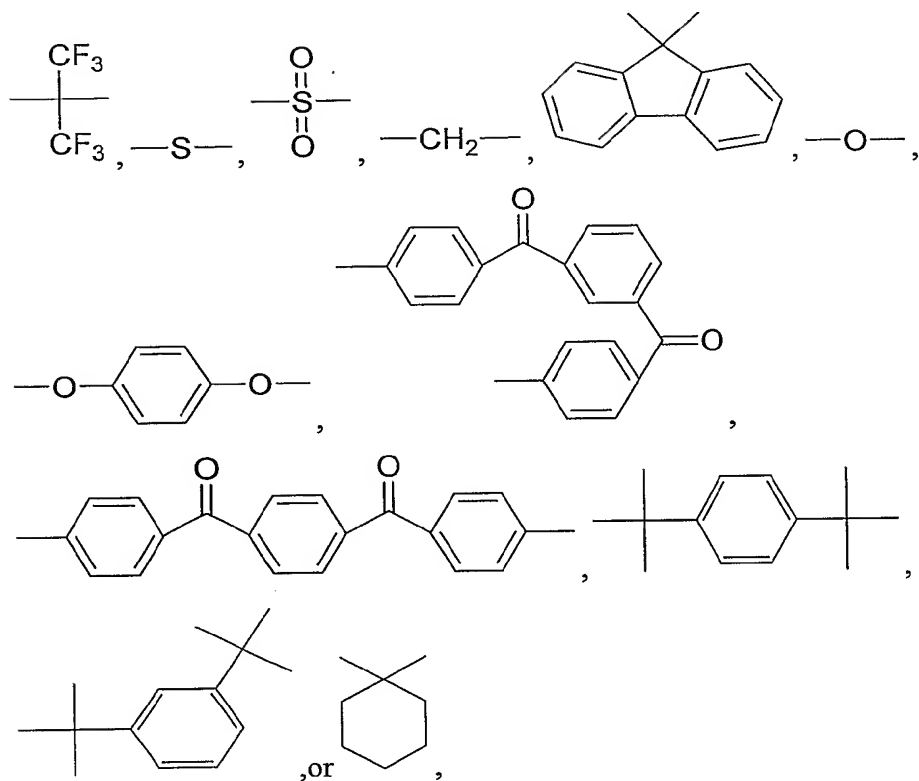
In general, the sulfonated copolymers include reaction products wherein $(a+c)=(b+d)$, a is from about 0.05 to about 0.95, b is from about 0.01 to about 0.95, c is from about 0 to about 0.95 and d is from about 0 to about 0.99. Preferably, a is from about 0.10 to about 1.00, b is from about 0.05 to about 0.85, c is from about 0 to about 0.90 and d is from about 0.15 to about 0.95. Most preferably, a is from about 0.20 to about 0.9, b is from about 0.10 to about 0.45, c is from about 0 to about 0.80 and d is from about 0.55 to about 0.90.

In another embodiment, the invention pertains to random sulfonated copolymers and proton exchange membranes having the formula

II



wherein R_1 or R_2 is a single bond, a cycloaliphatic of the formula C_nH_{2n-2} ,



where R_3 is aryl ketone, aryl sulfone, aryl nitrile, and substituted aryl nitrile.

wherein a, b, c and d are mole fractions of the monomer present in the copolymer where each are independently, from 0.01 to 1; and

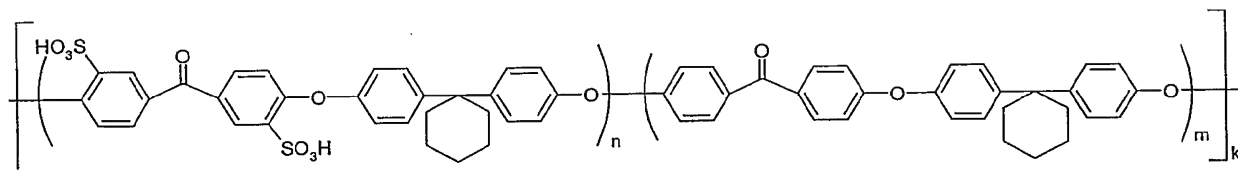
wherein X is a cation or a hydrogen atom.

- 10 In the sulfonated copolymer, a, b, c and d are mole fractions for each monomer present in the copolymer, each independently from 0.01 to about 1 and X is a cation or a hydrogen atom. In a preferred embodiment, R_1 is cyclohexyldyl, and R_2 is fluorenyl.

- 15 In general, the sulfonated copolymers include reaction products wherein $(a+c)=1.00$, $(b+d)=1.00$, a is from about 0.05 to about 1.00, b is from about 0.01 to about 1.00, c is from about 0 to about 0.95 and d is from about 0 to about 0.99. Preferably, a is from about 0.10 to about 1.00, b is from about 0.05 to about 0.85, c is from about 0 to about 0.90 and d is from about 0.15 to about 0.95. Most preferably, a is from about 0.20 to

about 1.00, b is from about 0.10 to about 0.45, c is from about 0 to about 0.80 and d is from about 0.55 to about 0.90.

A particularly preferred random copolymer is



$$n = 1 \sim 20$$

$$m = 0 \sim 50$$

$$k = 50 \sim 150$$

$$\text{sulfonation degree } x = n/(n+m)$$

5

Polymer membranes may be fabricated by solution casting of the ion conductive copolymer. Alternatively, the polymer membrane may be fabricated by solution casting the ion conducting polymer the blend of the acid and basic polymer.

10

When cast into a membrane for use in a fuel cell, it is preferred that the membrane thickness be between 1 to 10 mils, more preferably between 2 and 6 mils, most preferably between 3 and 4 mils.

As used herein, a membrane is permeable to protons if the proton flux is greater than approximately 0.005 S/cm, more preferably greater than 0.01 S/cm, most preferably greater than 0.02 S/cm.

15

As used herein, a membrane is substantially impermeable to methanol if the methanol transport across a membrane having a given thickness is less than the transfer of methanol across a Nafion membrane of the same thickness. In preferred embodiments the permeability of methanol is preferably 50% less than that of a Nafion membrane, more preferably 75% less and most preferably greater than 80% less as compared to the Nafion membrane.

20

After the sulfonated random copolymer has been formed into a membrane (PEM), it may be used to produce a catalyst coated membrane (CCM). As used herein, a CCM comprises a PEM where at least one side and preferably both of the opposing sides of the PEM are partially or completely coated with catalyst layers. The catalyst is preferable a layer made of catalyst and ionomer. Preferred catalysts are Pt and Pt-Ru. Preferred ionomers include Nafion and other ion conductive polymers.

In general, anode and cathode catalysts are applied onto the membrane by well established standard techniques. For direct methanol fuel cells, platinum/ruthenium catalyst is typically used on the anode side while platinum catalyst is applied on the cathode side and platinum is applied on the cathode side. Catalysts may be optionally supported on carbon. The catalyst is initially dispersed in a small amount of water (about 100mg of catalyst in 1 g of water). To this dispersion a 5% Nafion solution in water/alcohol is added (0.25-0.75 g). The resulting dispersion may be directly painted onto the polymer membrane. Alternatively, isopropanol (1-3 g) is added and the dispersion is directly sprayed onto the membrane. The catalyst may also be applied onto the membrane by decal transfer, as described in the open literature (*Electrochimica Acta*, 40: 297 (1995)).

The CCM is used to make MEA's. As used herein, an MEA refers to an ion conducting polymer membrane made from a CCM according to the invention in combination with anode and cathode electrodes positioned to be in electrical contact with the catalyst layer of the CCM.

The electrodes are in electrical contact with a membrane, either directly or indirectly, when they are capable of completing an electrical circuit which includes the polymer membrane and a load to which a electric current is supplied. More particularly, a first catalyst is electrocatalytically associated with the anode side of the membrane so as to facilitate the oxidation of organic fuel. Such oxidation generally results in the formation of protons, electrons, carbon dioxide and water. Since the membrane is substantially impermeable to organic fuels such as methanol, as well as carbon dioxide, such components remain on the anodic side of the membrane. Electrons formed from the electrocatalytic reaction are transmitted from the cathode to the load and then to the

anode. Balancing this direct electron current is the transfer of an equivalent number of protons across the membrane to the anodic compartment. There an electrocatalytic reduction of oxygen in the presence of the transmitted protons occurs to form water. In one embodiment, air is the source of oxygen. In another embodiment, oxygen-enriched air is used.

The membrane electrode assembly is generally used to divide a fuel cell into anodic and cathodic compartments. In such fuel cell systems, an organic fuel such as methanol is added to the anodic compartment while an oxidant such as oxygen or ambient air is allowed to enter the cathodic compartment. Depending upon the particular use of a fuel cell, a number of cells can be combined to achieve appropriate voltage and power output. Such applications include electrical power sources for residential, industrial, commercial power systems and for use in locomotive power such as in automobiles. Other uses to which the invention finds particular use includes the use of fuel cells in portable electronic devices such as cell phones and other telecommunication devices, video and audio consumer electronics equipment, computer laptops, computer notebooks, personal digital assistants and other computing devices, GPS devices and the like. In addition, the fuel cells may be stacked to increase voltage and current capacity for use in high power applications such as industrial and residential services or used to provide locomotion to vehicles. Such fuel cell structures include those disclosed in U.S. Patent Nos. 6,416,895, 6,413,664, 6,106,964, 5,840,438, 5,773,160, 5,750,281, 5,547,776, 5,527,363, 5,521,018, 5,514,487, 5,482,680, 5,432,021, 5,382,478, 5,300,370, 5,252,410 and 5,230,966.

Such CCM and MEM's are generally useful in fuel cells such as those disclosed in U.S. Patent Nos. 5,945,231, 5,773,162, 5,992,008, 5,723,229, 6,057,051, 5,976,725, 5,789,093, 4,612,261, 4,407,905, 4,629,664, 4,562,123, 4,789,917, 4,446,210, 4,390,603, 6,110,613, 6,020,083, 5,480,735, 4,851,377, 4,420,544, 5,759,712, 5,807,412, 5,670,266, 5,916,699, 5,693,434, 5,688,613, 5,688,614, each of which is expressly incorporated herein by reference.

In another aspect, the invention relates to methods for the preparation of the ion conducting (e.g., sulfonate) random copolymers that are useful as polymer electrolyte membranes. In general, the methods to prepare the include combining a first monomer

having at least one ion conducting group such as a sulfonate group with a second comonomer. The first monomer should have at least two leaving groups and the second comonomer should have at least two groups that can displace at least one leaving group of the first monomer. A third comonomer is included that has at least two leaving groups, such that at least one of the displacing groups of the second comonomer can displace at least one of the leaving groups of the third comonomer.

In a particular embodiment for the preparation of such polymers, the process further includes the step of combining a fourth comonomer having at least two displacing groups that can react with the leaving groups of either the first comonomer or the third comonomer.

The term "leaving group" is intended to include those functional moieties that can be displaced by a nucleophilic moiety found, typically, in another monomer. Leaving groups are well recognized in the art and include, for example, halides (chloride, fluoride, iodide, bromide), tosyl, mesyl, etc. In certain embodiments, the monomer has at least two leaving groups, which are "para" to each other with respect to the aromatic monomer to which they are attached.

The term "displacing group" is intended to include those functional moieties that can act typically as nucleophiles, thereby displacing a leaving group from a suitable monomer. The result is that the monomer to which the displacing group is attached becomes attached, generally covalently, to the monomer to which the leaving group was associated with. An example of this is the displacement of fluoride groups from aromatic monomers by phenoxide or alkoxide ions associated with aromatic monomers.

EXAMPLES

Example 1

Sulfonated PEEK with Bisphenol A composition

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bisphenol A (9.128g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g),

anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175 to 180°C for 6h. The reaction mixture was precipitated with acetone or methanol to obtain the crude product, then washed with hot water four times. The dry polymer was dissolved in DMAC for 20% coating solution. The obtained 2mil thick membrane was soaked in 1.5M H₂SO₄ for 16hr (overnight) and then rinsed in DI water for several times until no H₂SO₄ residue was detected.

The polymer membrane was swollen in water at room temperature and the polymer membrane conductivity was measured by AC impedance. The polymer membrane was swollen in an 8M methanol aqueous mixture at 80 °C for 24 hours to measure the dimensional stability.

Methanol crossover was measured in 8M MeOH using H-Cell, and the permeation rate was obtained by gas chromatography analysis.

The membrane conductivity: 0.021S/cm, Swelling at 80C, 8M: 620% by area

8M-MeOH Cross-over : $6.9 \times 10^{-7} \text{ cm}^2/\text{sec}$.

Example 2

Sulfonated PEEK with 50% Bisphenol A and 50% Hydroquinone composition

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, bisphenol A (4.564g), hydroquinone (2.202g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The dry polymer was dissolved in DMAC for 20% coating solution. The obtained 2mil thick

membrane was soaked in 1.5M H₂SO₄ for 16hr (overnight) and then rinsed in DI water for several times until no H₂SO₄ residue was detected.

The membrane conductivity: 0.027 S/cm.

Example 3

5 Sulfonated PEEK with 4,4'-Thiodiphenol composition

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-thiodiphenol (8.728g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture DMSO and toluene
10 (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times.

The membrane conductivity: 0.021S/cm

15 *Example 4*

Sulfonated PEEK with 4,4'-(Hexafluoroisopropylidene)diphenol composition

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(hexafluoroisopropylidene)diphenol (13.452g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone
20 (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The dry
25 polymer was dissolved in DMAC for 20% coating solution. The obtained 2mil thick membrane was soaked in 1.5M H₂SO₄ for 16hr (overnight) and then rinsed in DI water for several times until no H₂SO₄ residue was detected.

The membrane conductivity: 0.020S/cm.

Example 5

Sulfonated PEEK with 50% 4,4'-(Hexafluoroisopropylidene) diphenol and 50% Hydroquinone composition

5 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(hexafluoroisopropylidene)diphenol (6.726g), hydroquinone (2.202g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The
10 mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The dry polymer was dissolved in DMAC for 20% coating solution. The obtained 2mil thick membrane was soaked in 1.5M H₂SO₄ for 16hr (overnight) and
15 then rinsed in DI water for several times until no H₂SO₄ residue was detected.

The membrane conductivity: 0.021 S/cm.

Example 6

Sulfonated PEEK with 4,4'-Cyclohexylidenebisphenol - hydroquinone composition (95/5)

20 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-cyclohexylidenebisphenol (10.1977g), hydroquinone (0.2202g), 4, 4'-difluorobenzophenone (6.1096g), sulfonated 4,4'-difluorobenzophenone (5.0664g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then
25 increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The dry polymer was dissolved in DMAC for 20% coating solution. The obtained 2mil

thick membrane was soaked in 1.5M H₂SO₄ for 16hr (overnight) and then rinsed in DI water for several times until no H₂SO₄ residue was detected.

The membrane conductivity: 0.017S/cm, Swelling at 80C, 8M: 120% by area

8M-MeOH Cross-over : 2.4×10^{-7} cm²/sec.

5 *Example 7*

This example discloses a random copolymer based on 4,4'-Cyclohexylidenebisphenol(BisZ)/Sulfonated Difluorobenzophenone(SBK)/Difluorobenzophenone(BK).

10 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-cyclohexylidenebisphenol (10.7344g), 4, 4'-difluorobenzophenone (6.546g), sulfonated 4,4'-difluorobenzophenone (4.222g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C
15 for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The conductivity and water up-take at room temperature are listed in table below.

Example 8

20 This example discloses a random copolymer based on 4,4'-Cyclohexylidenebisphenol(BisZ)/Sulfonated Difluorobenzophenone(SBK)/Difluorobenzophenone(BK).

25 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-cyclohexylidenebisphenol (10.7344), 4, 4'-difluorobenzophenone (6.3714g), sulfonated 4,4'-difluorobenzophenone (4.5598g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C

for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times. The conductivity and water up-take at room temperature are listed in table below.

Example 9

5 This example discloses a random copolymer based on 4,4'-Cyclohexylidenebisphenol(BisZ)/Sulfonated Difluorobenzophenone(SBK)/Difluorobenzophenone(BK).

10 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-cyclohexylidenebisphenol (10.7344g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the
15 crude product, then washed with hot water four times. The conductivity and water up-take at room temperature are listed in table below.

Molar Composition % (BisZ/SBK/BK)	Conductivity S/cm	Swelling %
Example 7	0.005	25
Example 8	0.007	35
Example 9	0.017	120

Example 10

20 Sulfonated PEEK with 20% Hydroquinone/80% 4,4'-Cyclohexylidenebisphenol composition.

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, hydroquinone (0.8808g), 4,4'-cyclohexylidenebisphenol (8.5875g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times.

The membrane conductivity: 0.030 S/cm, Swelling at 80C, 8M: 92 % by area
8M-MeOH Cross-over : $5.4 \times 10^{-7} \text{ cm}^2/\text{sec}$.

Example 11

Sulfonated PEEK with 50% Hydroquinone/50% 4,4'-Cyclohexylidenebisphenol composition

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, hydroquinone (2.202g), 4,4'-cyclohexylidenebisphenol (5.3672g), 4, 4'-difluorobenzophenone (5.6732g), sulfonated 4,4'-difluorobenzophenone (5.9108g), anhydrous potassium carbonate (7.2g) were dissolved in a mixture DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times.

The membrane conductivity: 0.033S/cm, 8M-MeOH Cross-over : $4.3 \times 10^{-7} \text{ cm}^2/\text{sec}$.

Example 12

SO₂-Z/35 (JC 58-68):

In a 500 mL three necked round flask, equipped with a mechanical stirrer, a thermometer probe connected with a nitrogen inlet, and a Dean-Stark trap/condenser, bis(4-

fluorophenyl)sulfone (BisS, 24.79 g, 0.0975 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SbisK, 22.16 g, 0.0525 mol), BisZ (40.25 g, 0.15 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of Toluene. The reaction mixture was slowly stirred under a slow nitrogen stream. After heating at ~85 °C for 1h and at ~120 °C for 1 h, the reaction temperature was raised to ~135 °C for 3 h, and finally to ~170 °C for 2 h. After cooling to ~70 °C with continuing stirring, the viscous solution was dropped into 1L of cooled methanol with a vigorous stirring. The noodle-like precipitates were cut and washed with di-water four times and dried at 80 °C overnight. The sodium form polymer was exchanged to acid form by washing the polymer in hot sulfuric acid solution (0.5 M) twice (1 h each) and in cold di-water twice. The polymer was then dried at 80 °C overnight and at 80 °C under vacuum for 2 days. This polymer has an inherent viscosity of 0.60 dl/g in DMAc (0.25 g/dl). It's one-day swelling in 8M Methanol at 80°C was 142%, cross-over in 8 M methanol was 0.009 mg.mil/cc.min.cm² (boiled), conductivity was 0.013 S/cm (non-boiled) and 0.041 S/cm (boiled).

Example 13

SO₂-Z/40 (JC58-72):

This polymer was synthesized in a similar way as described in example 1, using following compositions: bis(4-fluorophenyl)sulfone (BisS, 22.88 g, 0.090 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SbisK, 25.34 g, 0.060 mol), BisZ (40.25 g, 0.15 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of Toluene. This polymer has an inherent viscosity of 0.67 dl/g in DMAc (0.25 g/dl).

Example 14

CN-K-Z/35 (JC58-79):

This polymer was synthesized in a similar way a described in example 1, using the following compositions: BisK (10.69 g, 0.049 mol), 2,6-difluorobenzonitrile (5.86 g, 0.042 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 20.69 g, 0.049 mol), BisZ

(37.57 g, 0.14 mol), and anhydrous potassium carbonate (25.15 g, 0.18 mol), 270 mL of DMSO and 135 mL of toluene. This polymer has an inherent viscosity of 0.86 dl/g in DMAc (0.25 g/dl).

Example 15

5 FL/35 (JC58-11):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 14.18 g, 0.065 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 14.78 g, 0.035 mol), 9,9-bis(4-hydroxyphenyl)fluorene (35.04 g, 0.10 mol), anhydrous potassium carbonate (17.97 g,
10 0.13 mol), anhydrous DMSO (180 mL) and freshly distilled toluene (90 mL). This polymer has an inherent viscosity of 0.88 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 26%, cross-over in 8 M methanol was 0.013 mg.mil/cc.min.cm² (non-boiled) and 0.016 mg.mil/cc.min.cm² (boiled), conductivity was 0.010 S/cm (non-boiled) and 0.019 S/cm (boiled).

15 *Example 16*

FL/40 (JC58-43):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 19.64 g, 0.09 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 25.34 g, 0.06 mol), 9,9-bis(4-hydroxyphenyl)fluorene (52.56 g, 0.15 mol), and anhydrous potassium carbonate (26.95
20 g, 0.19 mol), 270 mL of DMSO and 135 mL of toluene. This polymer has an inherent viscosity of 0.77 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 35%, cross-over in 8 M methanol was 0.016 mg.mil/cc.min.cm² (non-boiled) and 0.016 mg.mil/cc.min.cm² (boiled), conductivity was 0.015 S/cm (non-boiled) and 0.023
25 S/cm (boiled).

Example 17

Z-FL/40 (JC58-51):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 18.33 g, 0.084 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 23.65 g, 0.056 mol), 1,1-bis(4-hydroxyphenyl)cyclohexane (BisZ, 18.78 g, 0.070 mol), 9,9-bis(4-hydroxyphenyl)fluorene (FL, 24.53 g, 0.070 mol), and anhydrous potassium carbonate (25.15 g, 0.18 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 0.97 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 54%, cross-over in 8 M methanol was 0.015 mg.mil/cc.min.cm² (non-boiled) and 0.025 mg.mil/cc.min.cm² (boiled), conductivity was 0.018 S/cm (non-boiled) and 0.042 S/cm (boiled).

Example 18

FL-O/35 (JC58-57):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 21.27 g, 0.0975 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 22.17 g, 0.0525 mol), 9,9-bis(4-hydroxyphenyl)fluorene (FL, 26.28 g, 0.075 mol), 4,4'-dihydroxydiphenyl ether (O, 15.16 g, 0.075 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of toluene. This polymer has an inherent viscosity of 1.21 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 50%, cross-over in 8 M methanol was 0.023 mg.mil/cc.min.cm² (non-boiled), conductivity was 0.030 S/cm (non-boiled) and 0.039 S/cm (boiled).

Example 19

Z-O/35 (JC58-58):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 21.27 g, 0.0975 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 22.17 g, 0.0525 mol), BisZ (20.12 g, 0.075 mol), 4,4'-dihydroxydiphenyl ether (O, 15.16 g, 0.075 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of toluene. This polymer

has an inherent viscosity of 1.61 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 117%, cross-over in 8 M methanol was 0.019 mg.mil/cc.min.cm² (non-boiled), conductivity was 0.026 S/cm (non-boiled) and 0.057 S/cm (boiled).

Example 20

5 FL-O/40 (JC58-59):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 19.64 g, 0.09 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 25.34 g, 0.06 mol), 9,9-bis(4-hydroxyphenyl)fluorene (26.28 g, 0.075 mol), 4,4'-dihydroxydiphenyl ether (15.16 g, 0.075 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of toluene. This polymer has an inherent viscosity of 1.50 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 72%, cross-over in 8 M methanol was 0.023 mg.mil/cc.min.cm² (non-boiled), conductivity was 0.026 S/cm (non-boiled) and 0.056 S/cm (boiled).

15 *Example 21*

AF-O/35 (JC58-65):

This polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 21.27 g, 0.0975 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 22.17 g, 0.0525 mol), 4,4'-(Hexafluoroisopropylidene)-diphenol (25.21 g, 0.075 mol), 4,4'-hydroxyphenyl ether (15.16 g, 0.075 mol), and anhydrous potassium carbonate (26.95 g, 0.19 mol), 270 mL of DMSO and 135 mL of toluene. This polymer has an inherent viscosity of 1.10 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 232%, cross-over in 8 M methanol was 0.020 mg.mil/cc.min.cm² (non-boiled) and 0.079 mg.mil/cc.min.cm² (boiled), conductivity was 0.024 S/cm (non-boiled) and 0.061 S/cm (boiled).

Example 22

MB/35 (JC58-77):

This polymer was synthesized in a similar way as described in example 1, using following compositions: BisK (17.02 g, 0.078 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 17.73 g, 0.042 mol), 2,5-dihydroxy-4'-methylbiphenol (MB, 24.03 g, 0.12 mol), and anhydrous potassium carbonate (21.56 g, 0.156 mol), 216 mL of DMSO and 108 mL of toluene. This polymer has an inherent viscosity of 1.07 dl/g in DMAc (0.25 g/dl).

Example 23

TPM/35 (JC58-81):

This polymer was synthesized in a similar way as described in example 1, using following compositions: BisK (9.93 g, 0.046 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 10.34 g, 0.024 mol), 4,4'-dihydroxytetraphenylmethane (24.67 g, 0.050 mol), and anhydrous potassium carbonate (12.57 g, 0.091 mol), 126 mL of DMSO and 63 mL of toluene. This polymer has an inherent viscosity of 1.01 dl/g in DMAc (0.25 g/dl).

Example 24

Z50-FL50/30 (JC58-123)

This polymer was synthesized in a similar way as described in example 1, using following compositions: BisK (19.85 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 16.47), 9,9-bis(4-hydroxyphenyl)fluorene (22.77 g), Bis Z (17.44 g) and anhydrous potassium carbonate (23.36 g), 240 mL of DMSO and 120 mL of toluene. This polymer has an inherent viscosity of 0.74 dl/g in DMAc (0.25 g/dl).

Example 25

Z75-FL25/30 (JC58-124)

This polymer was synthesized in a similar way as described in example 1, using following compositions: BisK (19.85 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 16.47), 9,9-bis(4-hydroxyphenyl)fluorene (11.39 g), Bis Z (26.16 g) and anhydrous potassium carbonate (23.36 g), 240 mL of DMSO and 120 mL of toluene. This polymer has an inherent viscosity of 0.63 dl/g in DMAc (0.25 g/dl).

Example 26

Z25-FL75/30 (JC58-125)

This polymer was synthesized in a similar way as described in example 1, using following compositions: BisK (19.85 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 16.47), 9,9-bis(4-hydroxyphenyl)fluorene (34.16 g), Bis Z (8.72 g) and anhydrous potassium carbonate (23.36 g), 240 mL of DMSO and 120 mL of toluene. This polymer has an inherent viscosity of 1.05 dl/g in DMAc (0.25 g/dl).

Example 27

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(1,4-phenyldiisopropylidene)bisphenol (17.30g), Bis K(7.0915g), S-Bis K(7.3885g), , anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 6h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.0168S/cm (0.0436 S/cm, boiled), swelling by area in 8M methanol: 67%, 8M methanol cross-over: 0.013 mg/min.ml.mls.

Example 28

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(1,4-phenyldiisopropylidene)bisphenol

(17.30g), Bis K(7.637g), S-Bis K(6.333g), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 6h. The reaction mixture precipitates from methanol to get the rude product.

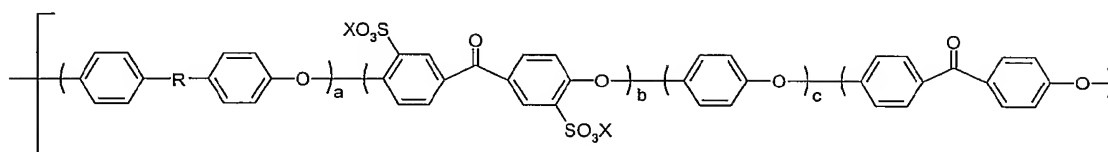
Conductivity: 0.00786S/cm (0.0315 S/cm, boiled), swelling by area in 8M methanol: 41%, 8M methanol cross-over: 0.011 mg/min.ml.mls.

All references cited throughout the specification, including those in the background, are specifically incorporated herein by reference in their entirety.

Although the present invention has been described with reference to preferred embodiments, persons skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

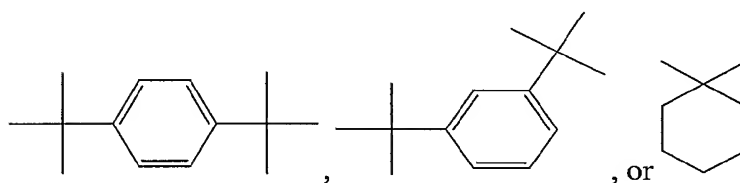
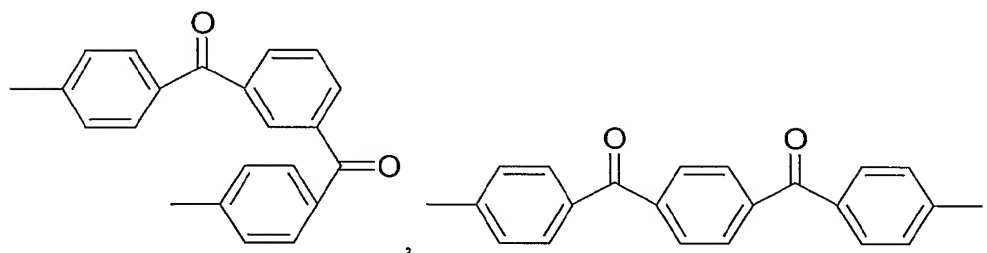
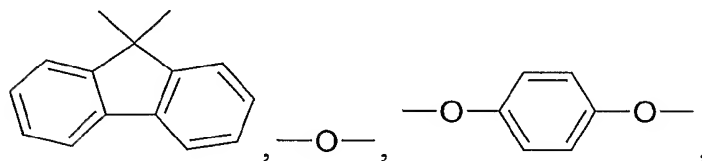
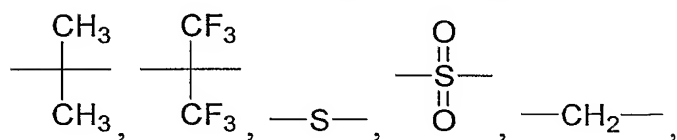
CLAIMS

1. A sulfonated copolymer having the formula:



5

wherein R is a single bond, a cycloaliphatic of the formula C_nH_{2n-2} ,



10

wherein a, b, c and d are mole fractions of the monomer present in the copolymer where each are independently, from 0.01 to 1; and

wherein X is a cation or a proton.

2. The sulfonated copolymer of claim 1, wherein R is isopropylidene or cyclohexylidene group.

3. A proton exchange membrane (PEM) comprising a sulfonated
5 copolymer of claim 1.

4. A catalyst coated membrane (CCM) comprising the PEM of claim 3 wherein all or part of at least one of the opposing surfaces of said membrane comprises a catalyst layer.

10

5. A membrane electrode assembly (MEA) comprising the CCM of claim
4.

6. A fuel cell comprising the MEA of claim 5.

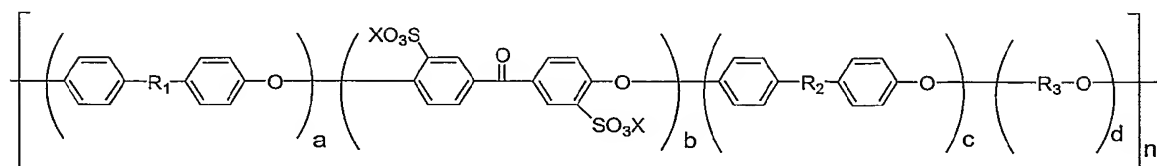
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7. An electronic device comprising the fuel cell of claim 6.

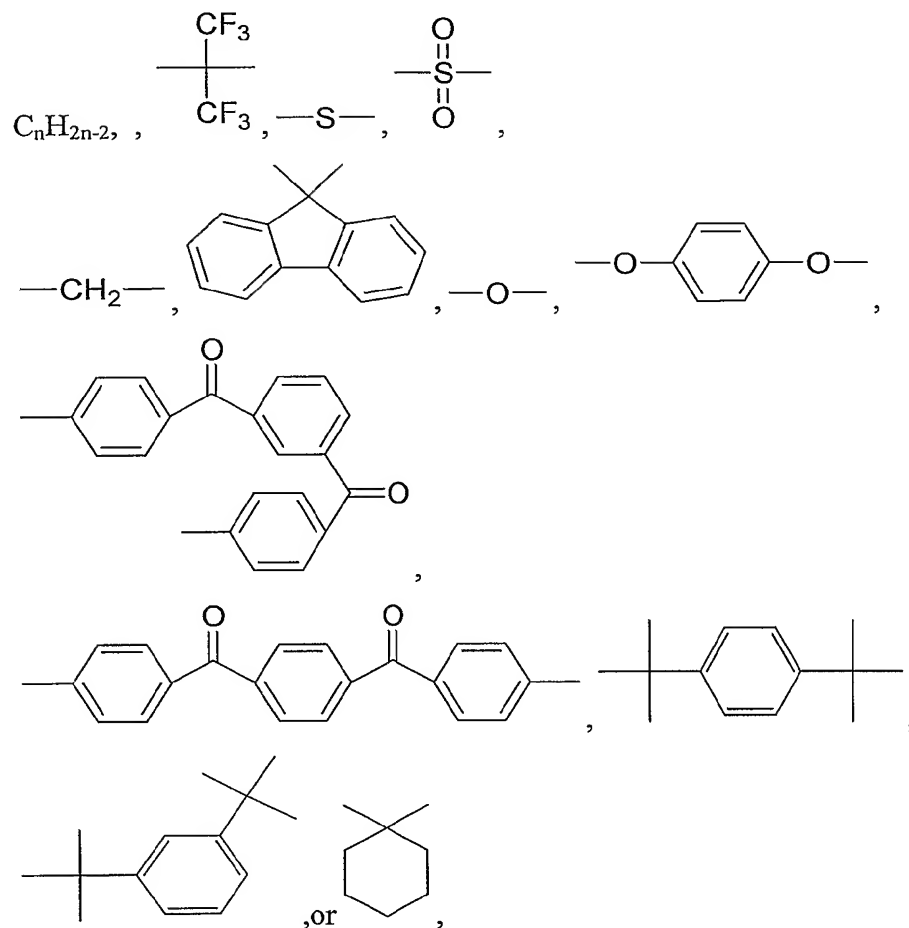
8. The proton exchange membrane of claim 3, wherein R is isopropyl or cyclohexyl.

20

9. A sulfonated copolymer having the formula:



wherein R₁ or R₂ is a single bond, a cycloaliphatic of the formula



where R₃ is aryl ketone, aryl sulfone, aryl nitrile, and substituted aryl nitrile.

wherein a, b, c and d are mole fractions of the monomer present in the copolymer where each are independently, from 0.01 to 1; and

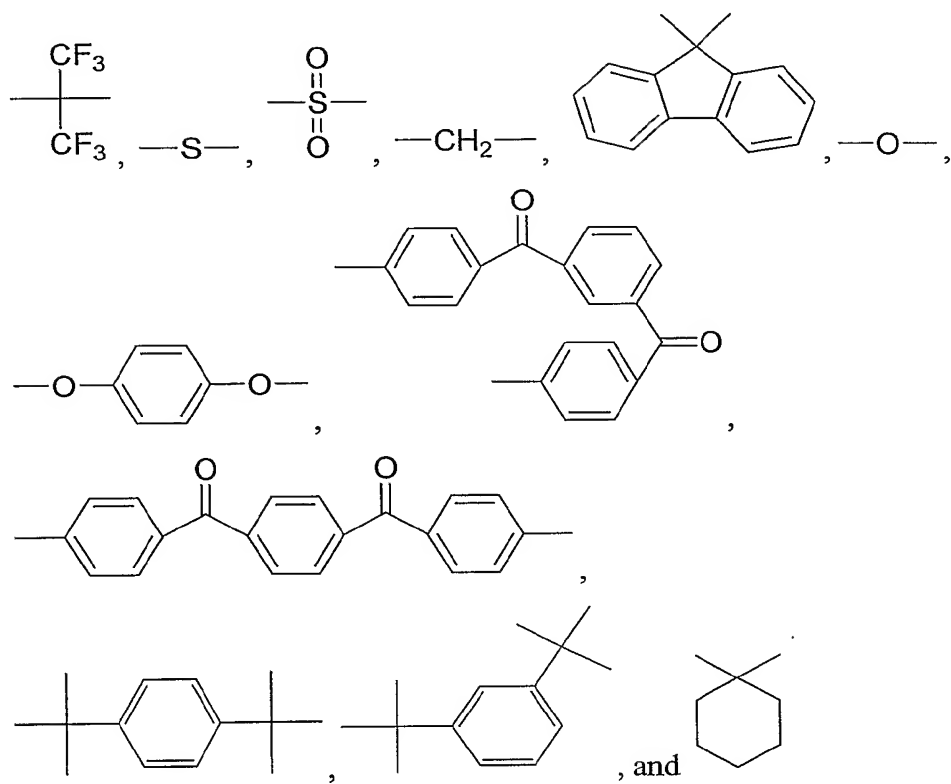
wherein X is a cation or a hydrogen atom.

10. The sulfonated copolymer of claim 8, wherein R₁ and R₂ are independently cyclohexyl or fluorenyl groups and R₃ is aryl ketone.

11. A proton exchange membrane (PEM) comprising the sulfonated copolymer of claim 9.

12. A catalyst coated membrane (CCM) comprising the PEM of claim 11 wherein all or part of at least one opposing surface of said PEM comprises a catalyst layer.
- 5 13. A membrane electrode assembly (MEA) comprising the CCM of claim 12.
14. A fuel cell comprising the MEA of claim 13.
- 10 15. An electronic device comprising the fuel cell of claim 14.
16. A method for the preparation of a sulfonated polymer, comprising the steps of
- 15 combining a first monomer having at least one sulfonate group and having at least two leaving groups with a second comonomer having at least two groups that can displace at least one leaving group of the first monomer and a third comonomer having at least two leaving groups, and a fourth comonomer having at least two displacing groups that can react with the leaving groups of either said first comonomer or said third comonomer when
- 20 said fourth comonomer such that at least one of the displacing groups of the second comonomer can displace at least one of the leaving groups of said third comonomer wherein
- said first comonomer forms $-\text{SO}_3-\text{Ar}-\text{C}(\text{O})-\text{Ar}-\text{SO}_3-\text{O}-$,
- said second comonomer forms $-\text{Ar}-\text{R}_1-\text{Ar}-\text{O}-$,
- 25 said third comonomer forms $-\text{Ar}-\text{R}_2-\text{Ar}-\text{O}-$, and
- said fourth comonomer forms $-\text{R}_3-\text{O}-$,

wherein R_1 and R_2 are independently selected from the group consisting of



5

R_3 is aryl ketone, aryl sulfone, aryl nitrile and substituted aryl nitrile.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/15178

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 16/36

US CL. : 526/347, 316, 312

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/347, 316, 312

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN: structure search

WEST 2.1: sulfonate, PEEK (or poly ether ether ketone)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2002/0091225 A1 [McGrath et al.] 11 July, 2002, abstract; col. 5, scheme 1.	1-16
A	GAN et al. "Synthesis and characterization of poly(ether ketone ketone)(PEEK)/sodium sulfonated poly(arylene ethylene ketone)(S-PAEK) block copolymers", Polymer International, 2001, Vol. 50, pages 812-816, especially page 814.	1-16
A	LIU et al. "Synthesis of poly(ether ether ketone)s with high content of sodium sulfonate groups as gas dehumidification membrane materials", Macromol. Rapid Commun. 2001, Vol. 22, pages 579-582, especially page 580	1-16

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

•	Special categories of cited documents:	"I"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

25 AUGUST 2003

Date of mailing of the international search report

30 OCT 2003

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/15178

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WANG et al. "Sodium sulfonate-functionalized poly(ether ether ketone)s", Macromol. Chem. Phys. 1998, Vol. 199, pages 1421-1426, especially page 1422.	1-16
A	XIAO et al. "Synthesis and characterization of novel sulfonated poly(arylene ether ketone)s derived from 4, 4'-sulfonyldiphenol", Polymer Bulletin, 2002, Vol. 48, pages 309-315, especially page 312.	1-16
A	LIU et al. "Novel sodium sulfonate-functionalized poly(ether ether ketone)s derived from 4,4'-thiodiphenol", Polymer, 2001, Vol. 42, pages 3293-3296, especially page 3294.	1-16